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Reactive Collisions and Final State Analysis of N- and O-involving
Reactions relevant to the Hypersonic Flight Regime

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Reactive Collisions and Final State Analysis of N- and O-involving Reactions relevant to the Hypersonic Flight Regime

Final Report on: Small-Molecule Reactions Relevant to the Hypersonic Flight Regime (July 1st 2017 to June 30th 2018)

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1 Summary

During this funding period the reactive dynamics of the [CNO] system has been investigated in-depth[1] and the rotational relaxation of Ar in N_2^+ has been analyzed in a quantitative fashion based on classical and quantum nuclear dynamics studies.[2]

2 Results

2.1 The Reactive Dynamics of the [CNO] System

Carbon, nitrogen and oxygen are among the dominant elements in the planetary atmosphere and in the interstellar medium. Studies involving the collisions between C-, N- and O-containing species are important for high temperature combustion chemistry. The triatomic [CNO] system shows rich chemistry as varieties of reactive collisions are possible. Among those, the C + NO → O + CN, N + CO reactions play important roles in NO reburning and therefore removing the pollutant NO from the atmosphere.[3] Reactive collisions between $C(^3P)+NO(X^2\Pi)$ yield $O(^3P)+CN(X^2\Sigma^+)$ and $N(^2D)+CO(X^1\Sigma^+)$ adiabatically on the ^2A surface, while nitrogen can be formed in its ground electronic state (^4S) on the ^4A surface.

The [CNO] system exhibits the Renner-Teller effect. For linear geometries the $^2A'$ and $^2A''$ PESs become degenerate and correspond to a $^2\Pi$ symmetry. However, for bent geometries the $^2\Pi$ symmetry splits into $^2A'$ and $^2A''$ states. Thus for excited vibrational states there is a possibility of nonadiabatic transitions between the $^2A'$ and $^2A''$ states. There are crossings between the doublet and quartet PESs in the N+CO product channel and these states are coupled via spin-orbit interactions which can lead to transitions between them. Thus inclusion of nonadiabatic effect in the dynamics of C+NO reaction may provide additional insights into the branching ratio of the products and the reaction paths. As the C+NO reaction is also important in combustion chemistry and NO plays a crucial role in the chemistry near the surface of a space vehicle during atmospheric re-entry,[4] studying the dynamics for this reaction at temperature relevant to the hypersonic flight regime will help to build a computational model of those situations. Here, the particular focus is on determining (a) accurate PESs for the $^2A'$, $^2A''$ and $^4A''$ symmetries for [CNO] based on high level *ab initio* calculations, (b) to use a robust method, the reproducing kernel Hilbert space (RKHS) for interpolation of the PES, and (c) to study the dynamics for a range of temperatures with a particular focus on conditions relevant to the hypersonic flight regime by including and excluding nonadiabatic effects in the dynamics.

We have computed new, global PESs have been constructed for the $^2A'$, $^2A''$, and $^4A''$ symmetries for the [CNO] system from a large number (> 50000) of MRCI+Q/aug-cc-pVTZ energies

using the reproducing kernel Hilbert space (RKHS) technique.[1] All possible product channels are described with the correct asymptotic behavior (R^{-6}) for neutral-neutral interactions. The reaction dynamics for the C+NO reaction are characterized using quasiclassical trajectory simulations which are validated vis-a-vis time independent quantum mechanical (TIQM) scattering calculations. Rate coefficients for the reaction are calculated over a wide range of temperatures, ranging from 15 K to 5000 K using both, adiabatic and nonadiabatic QCT simulations. Distributions of product states are calculated for the C+NO reaction at 0.06 and 0.23 eV of collision energies using QCT method. These allow validation of the QCT simulations by direct comparison with experiments.[5, 6, 7, 8] From the validated simulations, we further investigate the dynamics at conditions corresponding to high-temperature (5000 – 20000 K) hypersonic flow by determining corresponding thermal rates, distributions of products and vibrational relaxation as experiments at these extreme conditions are difficult or even impossible. Simulations with and without nonadiabatic transitions within the Landau-Zener[9, 10] formalism are carried out.

The total rate coefficients for the reaction are presented in Figure 1 for temperatures between 15 and 4000 K and compared with the available experimental[6, 7, 8] and theoretical[11] results. The rates from adiabatic QCT simulations (red line) were carried out separately on the three PESs considered in this work. Very good agreement between computations and the experimental results is found for $T > 50$ K in Figure 1. As the temperature decreases the computations deviate from the experimental results. A similar trend was also found in Ref. [11]. This may be be in part because the experiments for $T > 50$ K were carried out in Argon or N_2 as the buffer gas whereas for temperatures below 30 K Helium was used. Conversely, it is possible that the QCT simulations at the lowest temperatures ($T < 50$ K) miss contributions due to quantum corrections. The total rate coefficients calculated using TSH calculations following the Landau-Zener model are also presented in Figure 1 (indigo line). Both the adiabatic and the TSH rate constants show similar trend over the entire temperature range. However, The TSH rates overestimate the adiabatic results for high temperatures and underestimate it at low T. Below 50 K, both the adiabatic and the TSH approach can not describe the low temperature rates for this reaction.

The branching ratio as a function of temperature (CN vs. CO production) is presented in Figure 2 (a) and compared with experimental values along with the theoretical results from Ref. [11]. Two different experiments are available: one at 300 K and a second one for aa temperature range of 2400 to 4000 K.[7, 8] They show that the branching ratio is almost $T-$independent although the error bar for the 300 K measurement is large. Although the branching ratio from simulations without nonadiabatic transitions computed in this work is larger than the theoretical work of Ref. [11], it underestimates the experimental value. Including nonadiabatic transitions leads to improved theoretical results which agree with the experiments to within statistical errors.[7, 8]

Considering the C(^{3}P) + NO(X$^2\Pi$) $\rightarrow$ N(^{2}D)/N(^{4}S) + CO(X$^1\Sigma^+$) channel in particular, the predicted branching ratio for generation of N(^{2}D) vs. N(^{4}S) as a function of T ranges between 60 % and 80 % for adiabatic simulations and decreases to 50 %, almost independent of temperature, when nonadiabatic effects are included, see Figure 2 (b). Since adiabatically the ^{2}A states are only connected to N(^{2}D) and the ^{4}A state to N(^{4}S), this branching ratio reflects the population statistics and the reaction barriers. With TSH included, population
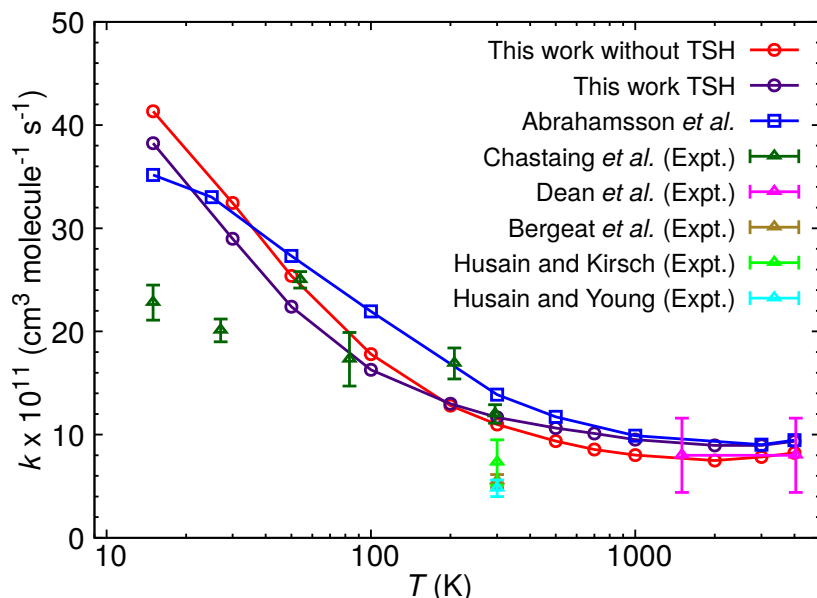
Figure 1: Total rate coefficients for the $C(^3P) + NO(X^2\Pi) \rightarrow O(^3P) + CN(X^2\Sigma^+)$, $N(^2D)/N(^4S) + CO(X^1\Sigma^+)$ over a range of temperatures from 15 – 4000 K. Theoretical[11] and experimental[12, 13, 6, 7, 8] results reported in literature are also plotted.

from the ^2A state can transfer to the ^4A PES increasing the amount of $N(^4S)$ created. This may provide a sensitive experimental probe of the importance of nonadiabatic effects in this reaction.

To explore the effect of including nonadiabatic transitions through surface hopping on the branching ratios for this reaction, the rate coefficients for CN and CO formation with and without TSH simulations are reported in Figure 2 (c top) and (c bottom). Including TSH in the dynamics substantially increases CO formation, whereas it slightly reduces the probability for CN formation. This eventually leads to a branching ratio which is close to the experimental value at 300 K.

The work[1] provides a comprehensive characterization of the $C(^3P) + NO(X^2\Pi) \rightarrow O(^3P) + CN(X^2\Sigma^+)$, $N(^2D)/N(^4S) + CO(X^1\Sigma^+)$ reactions using fully-dimensional PESs represented as a RKHS for the $^2A'$, $^2A''$, and $^4A''$ states. The use of quasiclassical trajectory simulations is justified by direct comparison with results from quantum simulations. For the experimentally characterized temperature range favorable agreement between computations and experiments is found for the rate coefficients, branching ratios, and final state distributions. Compared to adiabatic simulation, inclusion of nonadiabatic transitions between different electronic states for the reaction lead to a better agreement with the experimental branching ratios. For temperatures relevant to the hypersonic flight regime, the rate coefficients and vibrational relaxation times were determined and empirical expressions are provided which can be used in reaction network modeling.
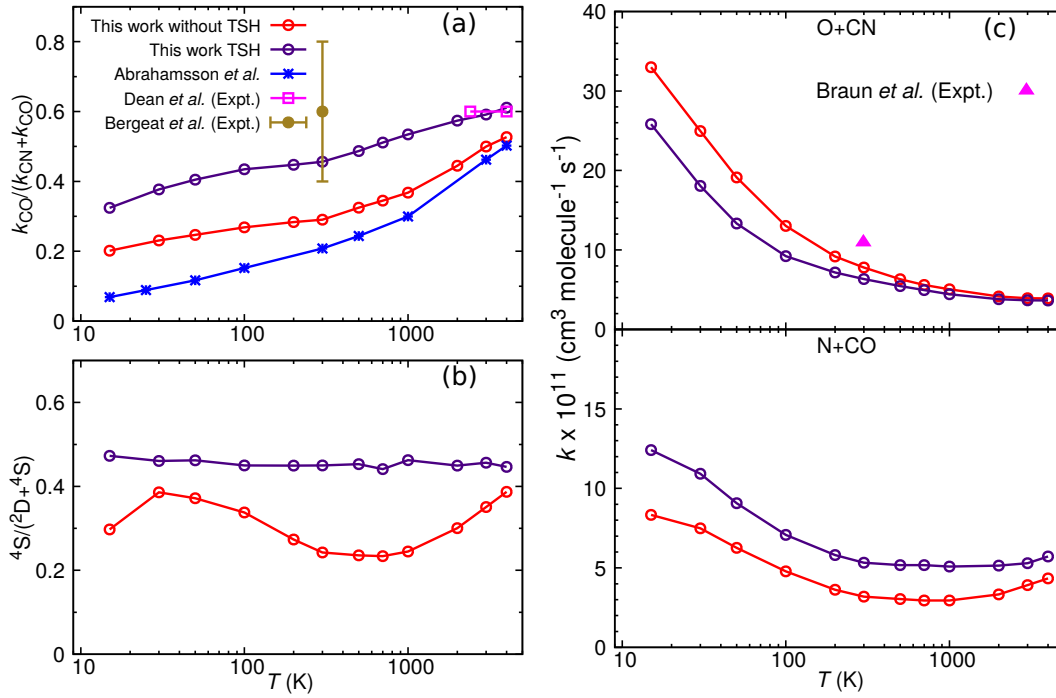
Figure 2: Branching ratios of (a) CO and CN products, and (b) ^{2}D and ^{4}S states of N in the N+CO channel, and (c) rate coefficients for the (top panel) C(^{3}P) + NO(X$^2\Pi$) → O(^{3}P) + CN(X$^2\Sigma^+$) and (bottom panel) N(^{2}D)/N(^{4}S) + CO(X$^1\Sigma^+$) reaction for $15 \leq T \leq 4000$ K, compared with available experimental[7, 8, 14] and theoretical[11] results. Red and dark blue traces from the present work without and with TSH.

2.2 Rotational Relaxation in Ar-N_2^+

Energy transfer between rotational, vibrational and electronic degrees of freedom is important in rarefied flows in the hypersonic regime.[15] One of the prototypical systems for such processes is the N_2^++Ar complex.[16, 17] Previous experiments showed that charge transfer from the molecule to the atom occurs only if N_2^+ is vibrationally excited and no charge transfer is possible for $N_2^+(v'=0)$.[16] One of the important technical aspects is whether or not quantum effects (tunneling, zero point motion) influence the results from computations. As this is a generally raised concern for molecular processes in small molecule reactions, the present work is relevant from a much broader perspective.[2]

The collision of N_2^+ molecules with Ar atoms is studied through quasi-classical trajectory molecular dynamics (QCT MD) and quantum simulations. Previous experiments reported inelastic rate coefficients 50 times smaller than those predicted by Langevin theory.[18] The efficiency of inelastic collisions in removing internal energy from collision partners is essential in experiments where cooling of the molecular ion is important. For the particular case of the $(v=0, j=6)$ state of the N_2^+ ion these early experiments indicated that rotational inelastic collisions would be insignificant. Contrary to that, recent quasiclassical trajectory simulations based on a UCCSD(T)/aug-cc-pVTZ and a zero point energy-corrected UCCSD(T)+ZPE potential energy surface, represented as a reproducing kernel Hilbert space (RKHS), suggested that inelastic collisions are non-negligible.[19] However, this computational study was based on single reference electronic structure calculations and QCT simulations which prompted the present work.

It is conceivable that due to the small difference in the electron affinity between $Ar(^1S)$ and $N_2(^1\Sigma_g^+)$ multireference effects become important, particularly in the long range of the potential energy surface which is important for the capture process and hence the early stages of the formation of the ion-atom complex. For the $N_2^+(X^2\Sigma_g^+) + Ar(^1S)$ system, the multi-reference character of the complex formed could play an important role, and effects beyond single-reference methods such as UCCSD(T) should be considered. Furthermore, quantum effects on the nuclear dynamics could also influence the rotational rates coefficients. These two aspects are the focus of the present work: The main goal of the present work is to study the $N_2^+(X^2\Sigma_g^+) + Ar(^1S)$ collision at low temperatures using multi-reference CI and UCCSD(T)-F12a electronic structure calculations and including quantum effects in the nuclear dynamics.

Quantum close coupling calculations on a new UCCSD(T)-F12a PES, represented as a reproducing kernel Hilbert space, for the Ar–N_2^+ have been carried out.[2] Furthermore, QCT calculations have been run on the same PES to directly compare with the QM results. For inelastic transitions, the agreement between quantum and classical results is good. However, irrespective of the PES used and whether the nuclear motion is treated with classical or quantum mechanics, the probability and rate for inelastic rotational excitation of the N_2^+ ion after collision with Ar is typically larger by one order of magnitude compared to experiment. New single-molecule experiments using quantum controlled initial states as is possible in Coulomb crystals[20, 21] and which are directly sensitive to the final state population would be valuable as there is no collisional mechanism that currently explains the conservation of the rotational quantum number found in the experiments carried out so far for this pivotal system. As quantum effects were found to be negligible in the present case (low j quantum number,
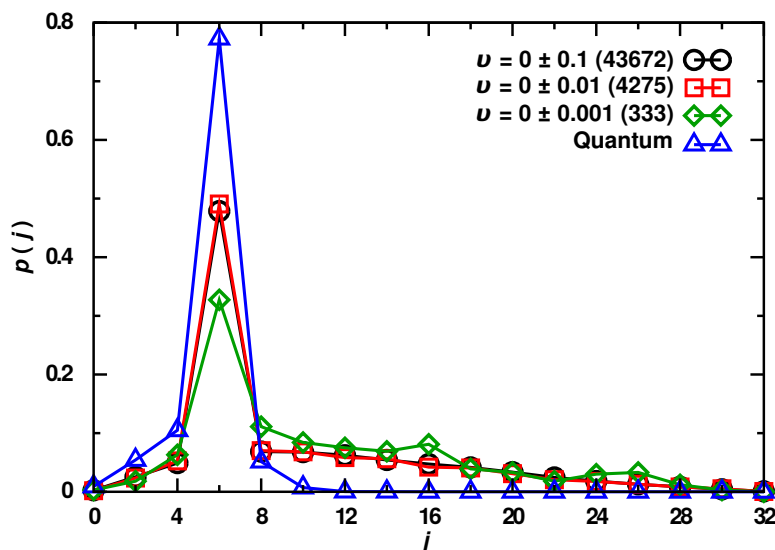
Figure 3: Fractional occupation of j states after the collision for different conservation criteria from QCT. The results of the quantum calculation are shown in blue. For the QCT simulations the numbers in bracket show how many of the 250000 trajectories meet the conservation criterion. Note that the simulations with frac(ν) = ±0.001 are probably not fully converged, see text.

temperature of $T = 90$ K) it is expected that QCT simulations are a valid approach for the much higher temperatures and quantum numbers involved in the hypersonic regime.

3   Publications from this Funding Period

- O. Denis-Alpizar, O. T. Unke, R. J. Bemish, and M. Meuwly
  Quantum and quasiclassical trajectory studies of rotational relaxation in Ar–N$_2^+$ collisions
  PCCP, 19, 27945 (2017)

- D. Koner, R. J. Bemish and M. Meuwly
  The C(^{3}P) + NO(X $^2\Pi$) → O(^{3}P) + CN(X $^2\Sigma^+$), N(^{2}D)/N(^{4}S) + CO(X $^1\Sigma^+$) reaction:
  Rates, branching ratios, and final states from 15 K to 20 000 K
  J. Chem. Phys., 094305 (2018)

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